

A26

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :  C09D 1/02, 5/02		A1	(11) International Publication Number: <b>WO 98/56861</b>  (43) International Publication Date: 17 December 1998 (17.12.98)																																																												
<p>(21) International Application Number: PCT/US98/12152</p> <p>(22) International Filing Date: 8 June 1998 (08.06.98)</p> <p>(30) Priority Data: 08/871,062 9 June 1997 (09.06.97) US</p> <p>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/871,062 (CIP) Filed on 9 June 1997 (09.06.97)</p> <p>(71) Applicants (for all designated States except US): HERBERTS GMBH [DE/DE]; Christbusch 25, D-42285 Wuppertal (DE). MICHELIN RECHERCHE ET TECHNIQUE S.A. [CH/CH]; Route Louis Braille 10 et 12, CH-1763 Granges-Paccot (CH).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): FEENEY, Carrie, A. [US/US]; 23 Kershaw Court, Bridgewater, NJ 08807 (US). FARRELL, Michele [US/US]; 1309 Beverly Avenue, Bethlehem, PA 18018 (US). McCARLEY, James, A. [US/US]; 24 Marudy Drive, Clinton, NJ 08809 (US). HUBBARD, Michael, A. [US/US]; 25 Oswestry Way, Somerset, NJ</p>		<p>08873 (US). GOLDBERG, Harris, A. [US/US]; 3 Emil Court, Edison, NJ 08820 (US). LU, Mengshi [CN/US]; 1275 Rock Avenue #FF4, North Plainfield, NJ 07060 (US). WARD, Bennett, C. [US/DE]; Altkonigstrasse 38, D-61462 Königstein (DE).</p> <p>(74) Agents: BAK, Mary, E. et al.; Howson and Howson, Spring House Corporate Center, P.O. Box 457, Spring House, PA 19477 (US).</p> <p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>																																																													
<p>(54) Title: AQUEOUS COATING COMPOSITION OF A POLYMER AND EXFOLIATED PLATELET FILLER</p> <p>(57) Abstract</p> <p>An aqueous barrier coating mixture is comprised of a non-elastomeric polymer present in said mixture at between about 0.25 to 28 % by weight; and a dispersed layered filler with an aspect ratio greater than 25, present in said mixture at between about 0.25 to about 10 % by weight, wherein the solids content of the mixture is less than about 29 %. In the dried coating, the polymer is present at a minimum of about 35 % by weight, and the dispersed layered filler is present at a minimum of at least 5 % by weight. The filler in the dried coating imparts an effective aspect ratio greater than 25, preferably greater than 50. This dried coating form provides a reduction in gas, vapor or chemical permeability greater than 5-fold that of the dried, unfilled polymer alone. Methods of coating substrates, which are rigid or flexible and elastomeric, to produce coated substrates, as well as free-standing films and membranes utilize these barrier coating mixtures.</p>																																																															
<table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>Volume fraction filler</th> <th>Permeability reduction (Aspect Ratio 25)</th> <th>Permeability reduction (Aspect Ratio 50)</th> <th>Permeability reduction (Aspect Ratio 75)</th> <th>Permeability reduction (Aspect Ratio 100)</th> </tr> </thead> <tbody> <tr> <td>0.00</td> <td>0</td> <td>0</td> <td>0</td> <td>0</td> </tr> <tr> <td>0.02</td> <td>20</td> <td>10</td> <td>5</td> <td>5</td> </tr> <tr> <td>0.04</td> <td>40</td> <td>20</td> <td>10</td> <td>10</td> </tr> <tr> <td>0.06</td> <td>60</td> <td>30</td> <td>15</td> <td>15</td> </tr> <tr> <td>0.08</td> <td>80</td> <td>45</td> <td>25</td> <td>25</td> </tr> <tr> <td>0.10</td> <td>100</td> <td>60</td> <td>40</td> <td>40</td> </tr> <tr> <td>0.12</td> <td>120</td> <td>75</td> <td>55</td> <td>55</td> </tr> <tr> <td>0.14</td> <td>140</td> <td>90</td> <td>70</td> <td>70</td> </tr> <tr> <td>0.16</td> <td>160</td> <td>105</td> <td>85</td> <td>85</td> </tr> <tr> <td>0.18</td> <td>180</td> <td>120</td> <td>100</td> <td>100</td> </tr> <tr> <td>0.20</td> <td>200</td> <td>135</td> <td>115</td> <td>115</td> </tr> </tbody> </table>				Volume fraction filler	Permeability reduction (Aspect Ratio 25)	Permeability reduction (Aspect Ratio 50)	Permeability reduction (Aspect Ratio 75)	Permeability reduction (Aspect Ratio 100)	0.00	0	0	0	0	0.02	20	10	5	5	0.04	40	20	10	10	0.06	60	30	15	15	0.08	80	45	25	25	0.10	100	60	40	40	0.12	120	75	55	55	0.14	140	90	70	70	0.16	160	105	85	85	0.18	180	120	100	100	0.20	200	135	115	115
Volume fraction filler	Permeability reduction (Aspect Ratio 25)	Permeability reduction (Aspect Ratio 50)	Permeability reduction (Aspect Ratio 75)	Permeability reduction (Aspect Ratio 100)																																																											
0.00	0	0	0	0																																																											
0.02	20	10	5	5																																																											
0.04	40	20	10	10																																																											
0.06	60	30	15	15																																																											
0.08	80	45	25	25																																																											
0.10	100	60	40	40																																																											
0.12	120	75	55	55																																																											
0.14	140	90	70	70																																																											
0.16	160	105	85	85																																																											
0.18	180	120	100	100																																																											
0.20	200	135	115	115																																																											

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

## AQUEOUS COATING COMPOSITION OF A POLYMER AND EXFOLIATED PLATELET FILLER

Field of the Invention

The present invention relates to novel barrier coating compositions, and  
5 particularly to coatings which have an enhanced reduction in gas, vapor and chemical  
permeability, and to methods of use thereof.

Background of the Invention

Barrier coatings which prevent, or reduce, contact of a selected substrate with  
a gas, vapor, chemical and/or aroma have been widely described, and such coatings  
10 are used in a variety of industries, e.g., the packaging industries, automobile  
industries, paint industries, tire industries etc. Some of these barrier mixtures or  
coatings have been proposed to contain plate-like structures to reduce permeability.  
See, for example, E. L. Cussler *et al*, J. Membrane Sci., 38:161-174 (1988); W. J.  
Ward *et al*, J. Membrane Sci., 55:173-180 (1991); U. S. Patent Nos. 4,528,235;  
15 4,536,425; 4,911,218; 4,960,639; 4,983,432; 5,091,467; and 5,049,609; and  
International patent application No. WO93/04118, published March 4, 1993, among  
others.

Despite the numerous disclosures of barrier coatings mixtures, most of the  
coatings useful in the industry which contain platelet type fillers are prepared by melt  
20 processing, in which solid polymer and solid filler are melted together and mixed at  
high shear rates. Such melt-processed coatings have 100% solids, and usually use less  
than about 3% by weight of the platelet fillers. Such coatings do not optimally reduce  
permeability.

There remains a need in the art for additional barrier coating mixtures and  
25 coated articles with improved permeability characteristics useful in a variety of  
industries.

Summary of the Invention

The present invention solves the problems of the prior art by providing an aqueous barrier coating composition which contains substantially dispersed exfoliated layered silicates in a non-elastomeric polymer. This coating, when dried, results in a barrier with a high effective aspect ratio, e.g., greater than 25 or greater than 50, and improved permeability characteristics, i.e., a greater increase in the reduction of permeability of the coating. Methods for coating articles with this coating mixture result in a dried coating with an effective aspect ratio greater than 50, and an increase of greater than 5-fold in the reduction of permeability of the coating in contrast to a coating formed of the unfilled polymer.

In one aspect, the present invention provides an aqueous barrier coating mixture which contains, (a) a non-elastomeric polymer; (b) a dispersed exfoliated layered platelet-like filler having an aspect ratio greater than 25; and (c) at least one surfactant. The solids content of the mixture is less than about 29%, and preferably between about 5% and 17%. Preferably, in the barrier coating mixture, the polymer is present at between about 0.25 to about 28% in liquid form and greater than about 35% by weight in the dried coating. The dispersed layered filler is present in the liquid coating mixture at between about 0.25% to about 10% by weight, and in the dried coating formed thereby, at greater than 5% by weight. The dried coating, in which the filler exhibits an effective aspect ratio of greater than about 25, and preferably greater than about 50, reduces the gas, vapor or chemical permeability greater than 5-fold that of the dried, unfilled polymer alone.

In one preferred embodiment, a mixture of this invention contains a water soluble polymer, preferably poly(vinyl) alcohol (PVOH). The filler is desirably a phyllosilicate, such as mica or vermiculite.

In another aspect, the invention provides a coating mixture which contains in its dried state between about 35% to about 95% by weight PVOH and between 5% to about 55% by weight of the filler and optionally a plasticizer other than water, which is present in a ratio of 1.5 parts by weight PVOH to 1 part by weight plasticizer.

In a further aspect, the invention provides a coated article comprising a substrate having on its surface a dried barrier coating of the invention, the coating comprising a non-elastomeric polymer and greater than 2% by volume of the layered filler having an effective aspect ratio greater than 50. The coating, in which the filler 5 preferably exhibits an effective aspect ratio of greater than about 50, reduces the gas, vapor or chemical permeation of the article by having a coating with the permeability reduced greater than 5-fold relative to an unfilled polymer coating.

In yet a further aspect, the invention provides a film comprising a dried coating mixture of the invention, containing a polymer and greater than 2% by volume of a 10 layered filler having an effective aspect ratio greater than 50, wherein the film is characterized by a reduction in gas, vapor or chemical permeability greater than 5-fold the permeability of a film formed of the polymer alone.

In still a further aspect, the invention provides a method for reducing the gas, vapor or chemical permeability of an article or substrate, which method comprises 15 coating the substrate with the barrier coating mixture described above, and drying the coating mixture on the substrate, wherein the coating provides an increase of greater than 5-fold in the reduction of permeability of the coating relative to a coating formed of the unfilled polymer.

Other aspects and advantages of the present invention are described in the 20 detailed description below and in the claims.

#### Brief Description of the Drawings

Fig. 1 is a "Cussler" model graph indicating the effective aspect ratios achieved by compositions of this invention. The graph plots reduction of permeability vs. volume percentages of filler in barrier coating mixtures of the present invention. 25 Cussler describes several models for the permeability reduction due to oriented layered fillers, which depend on the microstructure expected. For simplicity, this invention employs the equation:  $P_u/P = [1 + (a^2 X^2)/(1-X)]/(1-X)$ , where P is the permeability of the filled material,  $P_u$  is the permeability of the unfilled material; a is the aspect ratio of the filler particles; X is the volume fraction of the filler particles in

the coating. Cussler's theoretical curves for fillers with aspect ratios of 25, 50, 75, and 100 are present on the graph. Fig. 1 shows the experimental data points for the barrier coating mixtures of Examples 1-2 below. Effective aspect ratios can be estimated from the position of the data relative to the theoretical curves.

5      Detailed Description of the Invention

10     The present invention fills the unmet need in the art of barrier coatings by providing barrier coating mixtures which reduce the gas, vapor or chemical permeability of substrates. The coated articles, as well as free-standing films and membranes produced by these barrier coating mixtures are also provided by the invention.

*I.      Definitions*

15     As used herein, the term "mixture" or "coating mixture" is interpreted to include true aqueous solutions, as well as colloidal dispersions, suspensions, emulsions and latexes as they are conventionally defined. For example, by "colloidal dispersion or latex" is meant any dispersion or suspension of particles in water, the particles being of a size greater than molecular scale, e.g., about 0.001 to about 0.1 micron. An emulsion generally contains particles of about 0.05 to 1.0 microns in water. A "suspension" generally contains particles of greater than 1.0 micron in water.

20     A "barrier coating mixture" as used herein is meant an aqueous mixture containing dissolved or suspended solids and which is used to apply said solids to a substrate. According to this invention, once the "coating mixture" is dried, it is referred to as a "dried coating" or a "film".

The term "vapor barrier" implies a barrier to a liquid and its vapor.

25     Conventionally, a vapor is the gas in equilibrium with a liquid at atmospheric pressure. For simplicity, as used herein, the term "vapor barrier" can be interpreted to mean a barrier to gases and chemicals as well as traditionally defined vapors.

The term "gas barrier" includes a barrier to oxygen, nitrogen, carbon dioxide and other gases.

"Chemical barrier" includes a barrier to the migration or blooming of a molecule from one substrate to another or out of one substrate to that substrate's surface.

The term "substrate" or "article" coated by these coatings include,  
5 without limitation, polymeric films and sheets, rigid and semi-rigid containers, roofing materials, electrical appliances, industrial materials, flexible materials, elastomeric and highly elastic materials, such as rubber, and other surfaces.

The term "aspect ratio" is a characteristic of every platelet material in solid form. Aspect ratio is the product of the lateral dimension of a platelet filler  
10 particle, e.g., mica flake, divided by the thickness of the platelet. "High aspect ratio"  
refers to a platelet filler whose lateral dimension divided by thickness is greater than  
25. The aspect ratio of any filler is an inherent property of the selected filler. For  
example, MICROLITE® 963++ aqueous vermiculite solution [W. R. Grace] has a  
characteristic aspect ratio of about 10,000 to about 30,000, or dimensions of 10-30  
15  $\mu\text{m} \times 10\text{\AA}$ .

Intercalation is defined as the state of a coating composition in which polymer is present between each layer of a platelet filler. Intercalation can be defined by the detection of an X-ray line, indicating a larger spacing between vermiculite  
20 layers than in the original mineral. "Exfoliation" is defined for layered fillers as the complete separation of individual layers of the original particle, so that polymer  
completely surrounds each particle. Desirably so much polymer is present between  
each platelet, that the platelets are randomly spaced. No X-ray line appears because  
of the random spacing of exfoliated platelets. In some circumstances, the filler can  
exfoliate when dispersed in an aqueous or non-aqueous medium. This would result in  
25 a higher aspect ratio than that of a solid particle before dispersion.

The term "effective aspect ratio" relates to the behavior of the platelet  
filler when incorporated into a binder. The platelet may not exist in a single platelet  
formation, but in many forms, such as a bundle of 10-50 platelets or hundreds of  
platelets, referred to as agglomerates. If the platelets are not in the single layer form,  
30 the aspect ratio of the entire bundle or agglomerate is much lower than that of the

single layer particle. Therefore, the aspect ratio of the particles in a binder is referred to as an effective aspect ratio. The effective aspect ratio is determined by plotting the experimental data versus theoretical model, such as described by E. L. Cussler *et al*, J. Membrane Sci., 38:161-174 (1988). A graph of reduction in permeability versus the 5 volume % of filler in the binder generates theoretical curves for each effective aspect ratio. The graph predicts an effective aspect ratio for the experimental data. See Fig. 1.

## *II. The Barrier Coating Mixture*

10 A barrier coating mixture according to this invention is an aqueous mixture, i.e., a liquid, which includes, (a) a polymer present in the mixture at between about 0.25 to 28% by weight; and (b) a dispersed layered filler with an aspect ratio greater than 25 present in said mixture at between about 0.25 to about 10% by weight. The solids content of this liquid mixture is less than about 29%, and can range as low as about 5%.

15 Preferably the polymer is present in said mixture when dried at a weight percent of at least about 35%. The filler is preferably present in said mixture when dried at greater than about 5% by weight. The dried coating, in which the filler preferably exhibits an effective aspect ratio of greater than about 25, reduces the gas, vapor or chemical permeability greater than 5-fold that of the dried, unfilled polymer 20 alone. Preferably, the effective aspect ratio of the dried coating is greater than about 50, and even greater than about 75. These barrier coating mixtures result in coatings/films with reductions in permeability of up to about 85X relative to the unfilled polymer. These results are substantially higher than the prior art on other platelet filled barrier coatings.

25 The barrier coating mixtures of this invention are characterized by a balancing of several critical features, i.e., appropriate dispersion of the filler in the non-elastomeric polymer, orientation of the filler platelets in the non-elastomeric polymer, as well as high aspect ratio of the filler, in order to achieve the desired permeability reductions in the dried barrier coating. The barrier coating mixture of 30 this invention desirably contains an unusually low solids content, i.e., between about

1% and about 29% solids. A more desirable range of solids content is between about 5% to about 17 % solids. The solids content is an important consideration in the barrier coatings compositions and performance of the dried coatings because the solids content effects the dispersion of the high aspect ratio filler. If high total solids 5 content is used in the barrier coating composition, one would not achieve well dispersed filler, e.g., vermiculite, and the permeability reductions characteristic of the coatings of this invention, and reported in the examples and Fig. 1 herein, are not achieved. Thus, in this invention, the solids content of the mixture (less than about 29%) is maintained unexpectedly lower than that typically used in the coatings 10 industry in order to maintain good dispersion and achieve high reduction in permeability in the dried coating. Particularly, the preferred range of solid content (5-17%) is not predicted by the prior art teachings concerning barrier coatings formulations.

The unusually low solids contents described in barrier coatings 15 containing non-elastomeric polymers may be altered for other formulations of barrier coatings of this invention taking into account changes in electrolyte concentration, surfactants, grade and composition of vermiculite or other filler, and grade and composition of polymer in an aqueous carrier as described herein.

A. The Non-Elastomeric Polymer

20 Polymers useful in forming coating mixtures of this invention include non-elastomeric polymers selected generally from among many classes. The selected polymers may be crosslinkable polymers. Such polymers may also be curable polymers, partially cured polymers or uncured polymers. Such polymers include, without limitation, acetal for example, polyoxymethylene; acrylonitrile, for example, 25 polyacrylonitrile (PAN); acrylic resins, such as acrylonitrile-methyl acrylate copolymer (AMA); and cellulosic plastic, for example, cellophane film.

Fluoroplastic polymers, for example, ethylene-chlorotrifluoro-ethylene copolymer (ECTFE), ethylene-tetrafluoroethylene copolymer (ETFE), fluorinated ethylene-propylene copolymer (FEP), fluorinated polyethylene (FPE), 30 perfluoroalkoxy resin (PFA), polychlorotrifluoroethylene (CTFE),

polytetrafluoroethylene (TFE), polyvinyl fluoride (PVF), and polyvinylidene fluoride (PVDF) may also be useful. Other polymers useful in the coating mixture include ionomer; parylenes, such as polyparaxylylene; polyamides, such as nylon, amorphous nylon, nylon 6, nylon 66, nylon 6/66, nylon 66/610, nylon MXD6; polycarbonates (PC); polyesters, such as polybutylene terephthalate (PBT), polyethylene naphthalate (PEN), polyethylene terephthalate (PET), glycol modified polycyclohexylenedimethylene terephthalate (PCTG), polycyclohexylenedimethyl ethylene terephthalate (PETG), and liquid crystal polymer (LCP). Also useful are polyimides, and polyolefins, e.g., polyethylene (PE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultra low density ethylene-octene copolymer (ULDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), ethylene-alpha olefin copolymer (POP), ethylene-vinyl acetate (EVA), ethylene-vinyl alcohol copolymer (EVOH), polyethylene-acrylic acid copolymer (EAA), polyethylene-ionomer copolymer (PE-ionomer), polypropylene copolymer (PP copolymer), polybutylene, and polymethylpentene (PMP).

Still other polymers useful in the coating solutions of the invention include polyphenylene sulfide (PPS); polysulfone (PSO); poly(vinyl alcohol) (PVOH); styrenic resin, e.g., acrylonitrile-butadiene-styrene copolymer (ABS), acrylonitrile-styrene-acrylate copolymer (ASA), polystyrene (PS), general purpose polystyrene (GPPS), impact resistance polystyrene (IPS), styrene-acrylonitrile copolymer (SAN), styrene-butadiene block copolymer. Vinyl resins, such as polyvinyl chloride (PVC), polyvinyl chloride-polyvinylidene chloride copolymer (PVC-PVDC), polyvinylidene chloride (PVDC) may be used. Other such polymers include plastic alloys, e.g., polyethylene/polystyrene alloy (PE/PS); epoxy resins; and polypyrrole.

Preferably, the selected polymer is present in the dried coating mixture at a minimum of about 35% by weight of the dried compositions. The selected polymer is desirably water-soluble or capable of forming a solution, dispersion, latex or emulsion in water. Specifically exemplified below is a coating mixture of the invention employing as the water-soluble polymer poly(vinyl alcohol). Many suitable PVOH polymers exist of varying viscosities and molecular weights; one

of skill in the art may select the appropriate PVOH for the coating mixture based on the selection and weight percentages of the selected filler.

B. The Filler

The coating mixtures of this invention as described above also include a dispersed layered filler which, upon mixture, has an inherently high aspect ratio, which can range from about 25 to as high as about 30,000. The presently preferred filler is vermiculite. More particularly, a desirable vermiculite is 5 MICROLITE® 963++ water-based vermiculite dispersion (W.R. Grace) [see, EP Application No. 601,877, published June 15, 1994] which is a 7.5% by weight 10 aqueous solution of dispersed mica. One novel aspect of the mixtures of the present invention is the effective aspect ratio of the selected filler in the dried coating. According to this invention, in the dried coating, the filler remains substantially 15 dispersed, thereby having a "high effective aspect ratio", as shown in Fig. 1. Fig. 1 assumes high levels of orientation. The effective aspect ratio of the filler in the compositions of this invention is greater than 25 and preferably greater than about 50, although higher ratios may also be obtained. In the coating mixtures (the liquid), the layered filler is present at between about 0.25 to about 10% by weight of the total 20 mixture. In the dried coatings of this invention, the layered filler is present at a minimum of about 5% by weight of the dried coating.

25 In contrast to prior art coating mixtures in which high aspect ratio materials are employed and less than 5-fold reductions in permeability are achieved compared to the unfilled polymer, the compositions of the present invention, when dried, retain the filler in well-dispersed form, resulting in a high effective aspect ratio of the dried coating, and greatly increased reduction in permeability, as illustrated in Fig. 1.

30 MICROLITE vermiculite is the preferred filler because of its very high aspect ratio. The vermiculite plates have an average lateral size of between 10 and 30 microns. The plates are largely exfoliated in water, and thus their thickness is 1-2 nm. The aspect ratio of the filler in water dispersion is an average of 10,000-30,000. It is clear that many plates reassemble during the coating and drying process

of the present invention, thus reducing the effective aspect ratio achieved in the final coating. However, it is a great advantage to start with as large an aspect ratio as possible. Thus, the platelet filler selected for use in the present invention must have an aspect ratio greater than 25, and preferably, much greater than 25, e.g., 10,000 or 5 higher.

Although MICROLITE 963++ vermiculite (W. R. Grace) is preferred, good results may also be achieved with less exfoliated grades of MICROLITE vermiculite (i.e., grades 963, 923, and 903). Other layered silicates are also useful in the barrier coatings and films of this invention. The effectiveness of 10 other silicates in the barrier coating of this invention depends upon the lateral size of the platelets, the degree of exfoliation in water, and the degree to which they reassemble to form larger particles during the coating and drying process. Examples of other layered silicates include bentonite, vermiculite, montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, laponite, sauconite, magadiite, kenyaita, 15 ledikite and mixtures of the above silicates. The selection and use of other known silicates which have properties similar to those of MICROLITE vermiculite, as well as sufficiently high aspect ratios, are expected to be obvious to one of skill in the art following the teachings of this invention.

#### C. The Plasticizer

20 Optional ingredients of the coating mixture include a plasticizer other than water. When present, the plasticizer in the dried coating is in a ratio of 1.5 parts by weight polymer to 1 part by weight plasticizer. Plasticizers may readily be selected by those of skill in the art of barrier coatings. However, desirably, when the polymer selected is PVOH, plasticizers suitable for the preferred polymer PVOH may 25 include, without limitation, polyethylene glycol (PEG), ethylene glycol, diethylene glycol, triethylene glycol, glycerine, trimethylol propane, neopentyl glycol, triethanolamine, and ethoxylated phosphates. A commercially available plasticizer employed in the examples below is glucose [Sigma-Aldrich].

D. Surfactants and Other Additives

Coating mixtures of this invention also contain at least one or more than one suitable surfactant to reduce surface tension. Surfactants include materials otherwise known as wetting agents, anti-foaming agents, defoaming agents, 5 emulsifiers, dispersing agents, leveling agents etc. Surfactants can be anionic, cationic and non-ionic, and many surfactants of each type are available commercially. A suitable surfactant for inclusion in these compositions possesses a critical micelle concentration sufficiently low to ensure a dried coating in which the barrier properties are uncompromised by residual surfactant. Preferably, the surfactant(s) useful in the 10 methods and solutions of this invention are nonionic, particularly useful with a highly charged filler, such as vermiculite. Increase in ionic concentration of the compositions containing vermiculite, such as by the addition of a base to adjust pH, e.g., LiOH, NH<sub>4</sub>OH, and NaOH, can cause agglomeration of the filler, which adversely affects permeability reduction.

15 Embodiments of this invention include surfactants, such as a wetting agent. A desirable surfactant employed in the examples below is the non-ionic siloxane-based, Silwet® L-77 wetting agent [OSI Specialties, Inc.], among others. Other suitable surfactants may also be selected. The amount and number of 20 surfactants added to the coating solution or composition will depend on the particular surfactant(s) selected, but should be limited to the minimum amount of surfactant that is necessary to achieve wetting of the substrate while not compromising the performance of the dried coating. For example, typical surfactant amounts can be less than or equal to about 15% by weight of the dried coating.

25 Similarly, other optional components of the coating mixture include conventional agents to adjust pH to between about 8 to about 11, such as NH<sub>4</sub>OH, NaOH or LiOH, provided that care is taken to avoid agglomeration (as discussed above).

5           E.     The Carrier Liquid

The coating mixtures of this invention are preferably aqueous based mixtures. However, combinations of water with an organic carrier or organic solvent additives, may also be used as the carrier liquid.

10           F.     Embodiments of Barrier Mixtures

In one preferred embodiment, a coating mixture of this invention has a solids content of about 6% solids by weight, and contains in its dried state, about 41% by weight of the polymer; about 24% by weight of the filler; about 25% by weight of a plasticizer; and about 10% by weight of a surfactant. Examples 10 of coating mixtures according to this embodiment are described in Example 1 (wherein the polymer is PVOH; the filler, vermiculite; the plasticizer, glucose and the surfactant, Silwet® L-77) and in Example 2 (wherein the polymer is a terpolymer consisting of poly(vinylbutyral), poly(vinylacetate) and poly(vinylalcohol) with the same filler, surfactant and plasticizer). As one preferred embodiment, the coating 15 mixture comprises in its dried state at least about 35% by weight of the selected polymer, e.g., PVOH, and at least 5% by weight of the layered filler. These barrier coatings results in reductions in permeability of up to about 85X relative to the unfilled polymer. These results are substantially higher than the prior art on other platelet filled barrier coatings. See, e.g., Examples 1 and 2.

20           III.    *The Coated Article*

Once prepared as described in detail in Examples 1 and 2 below, the coating mixtures may be applied to a suitable substrate to reduce the permeability of the substrate to gas, vapor or chemical. The dried coating, in which the filler exhibits an effective aspect ratio of greater than about 25, reduces the gas, vapor or chemical 25 permeability greater than 5-fold that of the dried, unfilled polymer alone. Preferably, the effective aspect ratio of the dried coating is greater than about 50, and even greater than about 75.

Desirable substrates for coating with the coating mixtures of this invention may be rigid or semi-rigid substrates, suitable for coating with a mixture of 30 the invention containing a non-elastomeric polymer. Such substrates can be

automobiles or industrial parts, packaging materials, appliance surfaces, electrical parts and wires, roofing materials, etc. Possibly these coating mixtures may be employed to coat more flexible substrates as well.

The articles to be coated by the compositions of the invention may be 5 previously untreated or may have a variety of pre-treatments to their surfaces, depending upon the identity and utility of the article. For example, the article may have on at least one side a heat seal layer. Such heat seal layers may be made of an ethylene-propylene copolymer or ethylene-propylene-butylene terpolymer. Thus, the coating solution is applied on the surface of the heat seal layer. Alternatively, the 10 substrate or article may comprise a protective topcoat layer, such as polyurethane or Teflon®-type materials [DuPont] for abrasion resistance, etc. Such topcoats may be selected by one of skill in the art. The coatings of this invention may be applied over or under the topcoat layer.

Alternatively, the coating mixtures of the invention may be applied to a 15 releasable mold in order to form a film, rather than a coated article. The film thus consists of a dried mixture of the above-described polymer and greater than 2% by volume of the layered filler having an effective aspect ratio greater than 25, preferably greater than 50. The film, which may be in the form of a membrane, may itself be employed as a vapor, gas or chemical barrier layer for use in various laboratory 20 procedures, or as a glove or balloon material. Such a dried, free-standing film or membrane, is characterized by a reduction in gas, vapor or chemical permeability greater than 5-fold the permeability of a film formed of the dried polymer alone.

To form the coated article or free-standing film of this invention, the 25 coating mixtures of this invention may be applied to the selected surface or article by techniques including, without limitation, roll coating, spray coating, brush coating and dip coating techniques. Roll coating techniques include, but are not limited to, rod, reverse roll, forward roll, air knife, knife over roll, blade, gravure and slot die coating methods. General descriptions of these types of coating methods may be found in texts, such as *Modern Coating and Drying Techniques*, (E. Cohen and E. Gutoff, eds; 30 VCH Publishers) New York (1992) and *Web Processing and Converting Technology*

and Equipment, (D. Satas, ed; Van Nostrand Reinhold) New York (1984). Three dimensional articles may preferably be coated by the techniques which include, but are not limited to, spray coating or dip coating. The method of application is not a limitation on the present invention, but may be selected from among these and other 5 well-known methods by the person of skill in the art. However, the coating must be applied so that drying takes place on the substrate and not in the air (i.e. powder coating). If drying takes place during spraying or other means of application, agglomeration may occur.

The coating mixtures may be applied to a substrate or a mold at any 10 desired thickness, depending on the substrate, the purpose for which the coating is being applied and the ultimate use of the coated article. Thus, for example, the coating mixtures of the present invention may be applied to an article or substrate by the methods described above to form a dried coating of a thickness between about 0.1  $\mu\text{m}$  to about 100  $\mu\text{m}$  of dry coating. Such adjustments are well within the skill of the art 15 [see, e.g., Canadian Patent No. 993,738].

After coating, the coated article or mold may be dried at a selected 20 temperature, e.g., room temperature or greater than room temperature. The selection of the drying temperature, relative humidity, and convective air flow rates depends on the desired time for drying; that is, reduced drying times may be achieved at elevated air temperatures, lower relative humidity and higher rates of air circulation over the 25 drying coating surface. After drying, the exfoliated silicate filler particles are oriented within the non-elastomeric polymer (solution, emulsion, etc.) to a high degree parallel to each other and to the substrate surface. One of skill in the art can readily adjust the drying conditions as desired. The performance of the dried barrier coating is insensitive to drying temperatures over the range 25-125°C.

The dried coatings exhibit a surprising reduction in permeability 30 compared to the prior art and particularly compared to unfilled polymers. As evidenced in the Examples below, reductions in permeability caused by the dried coatings of this invention are shown to be up to 85 fold relative to the unfilled polymers alone. The evaluation of permeability of the coatings of the present

invention are determined using the following parameters. The oxygen transmission rate (OTR) of the dried coating on the article, or the free-standing film, is generally measured using conventional apparatus, such as a MOCON® OX-TRAN 2/20 module. OTR units are cc/m<sup>2</sup> day at 1 atmosphere, 0% relative humidity at 30°C.

5 The permeability of the coating is calculated by multiplying the OTR and coating thickness. Permeability units are cc mm/m<sup>2</sup> day atmosphere at 0% relative humidity at 30°C. If the coating is on a known substrate, the permeability of the known substrate is subtracted out using the following equation:

$$\text{Permeability of the barrier coating} = X_1 / [(1/\text{OTR}) - (X_2/P_{X2})], \text{ where } X_1$$

10 is barrier coating thickness; X<sub>2</sub> is substrate thickness and P<sub>X2</sub> is permeability of the substrate. The reduction in permeability from the unfilled polymer is calculated by dividing the permeability of the unfilled polymer by the permeability of the filled polymer. Reduction in permeability is unitless.

15 The invention is illustrated by the following examples, which are not intended to limit the scope of this invention.

#### EXAMPLE 1: Barrier Coating Containing PVOH As Polymer

An exemplary aqueous polymeric barrier coating solution according to this invention is prepared as follows, in which the polymer is poly(vinyl)alcohol (MW=61,000) and the filler is Microlite® dispersed mica.

20 In a 125 mL jar, 1.0 g of Mowiol® poly(vinyl) alcohol [Hoechst] is heated in 30 g water. This mixture is heated in a water bath while stirring on a stir plate until the PVOH is dissolved in the water. The resulting PVOH solution is cooled to room temperature and the following components are added to it: 7.8 g Microlite® 963++ in a 7.5% aqueous dispersion [W. R. Grace], 0.24 g Silwet® L-77 wetting agent [OSI Specialties, Inc.] and 0.6 g glucose [Sigma-Aldrich]. The resulting solution is stirred on a stir plate at room temperature for five minutes or until a homogeneous solution is achieved. This liquid coating mixture has a 6.1% solids content.

25 After this coating solution is applied to a butyl rubber substrate and allowed to dry, the coating contains 41% by weight PVOH, 24% by weight filler, 25% by weight

glucose and 10% by weight wetting agent. The oxygen transmission rate (OTR) is measured using a MOCON® OX-TRAN 2/20 module. The OTR is 4.3 cc/m<sup>2</sup> day @ 1 atmosphere, 0% RH, 30°C. Permeability of the composition is 0.025 cc mm/m<sup>2</sup> day atmosphere @ 0% RH, 30°C. The reduction in permeability of this coating is 41 times the reduction in permeability of the polymer alone.

5

#### EXAMPLE 2: Barrier Coating with Terpolymer

Another exemplary aqueous polymeric barrier coating solution according to this invention is prepared as follows, in which the polymer is 5% by weight of a terpolymer consisting of poly(vinylbutyral) (PVB) and poly(vinylacetate) (PVA) and 10 poly(vinylalcohol), and the filler is Microlite® dispersed mica.

In 125 mL jar, 1.0 g of Mowiol® terpolymer of PVB/PVA/PVOH (Hoechst) and 30g of distilled water are mixed and heated in a water bath while stirring on a stir plate until dissolved. The terpolymer solution is cooled and 7.8 g of Microlite® 963++ (7.5% solution, W.R. Grace), 0.24 g of Silwet L-77 (OSI Specialties, Inc.) and 15 0.6 g of glucose (Sigma-Aldrich) are added. The resulting solution is stirred on a stir plate. This solution has a 6.1% solids content.

15

After this coating solution is applied to a butyl rubber substrate and allowed to dry, the resulting coating has 41% by weight of the terpolymer, 24% by weight of the vermiculite, 25% by weight glucose, and 10% by weight of the Silwet L-77 surfactant. The oxygen transmission rate (OTR) is measured using a MOCON® OX-TRAN 2/20 module. The OTR is 1.2 cc/m<sup>2</sup> day @ 1 atmosphere, 0% RH, 30°C. Permeability of the composition is 0.012 cc mm/m<sup>2</sup> day atmosphere @ 0% RH, 30°C. The reduction in permeability of this coating is 85 times the reduction in permeability of the terpolymer alone.

25

Numerous modifications and variations of the present invention are included in the above-identified specification and are expected to be obvious to one of skill in the art. Such modifications and alterations to the compositions and processes of the present invention are believed to be encompassed in the scope of the claims appended hereto.

## WHAT IS CLAIMED IS:

1. An aqueous barrier coating mixture comprising:
  - (a) between about 0.25 to 28% by weight of a non-elastomeric polymer; and
    - (b) between about 0.25 to about 10% by weight of a dispersed exfoliated layered platelet filler having an aspect ratio greater than 25;wherein the solids content of said mixture is less than about 29%, and wherein said mixture, when dried, forms a coating that provides a reduction in gas, vapor or chemical permeability greater than 5-fold that of said dried polymer alone.
2. The mixture according to claim 1, wherein said solids content is between about 5% and 17%.
3. The mixture according to claim 1, which when dried, comprises
  - (a) said polymer present in said dried mixture at a weight percent of at least about 35%; and
    - (b) said dispersed layered filler present in said dried mixture at greater than about 5% by weight, and imparting to said dried mixture an effective aspect ratio greater than 50.
4. The mixture according to claim 3 wherein said effective aspect ratio is greater than 75.
5. The mixture according to claim 1 wherein said polymer is selected from the group consisting of acetal, acrylonitrile, acrylic resins, cellulosic plastic, fluoroplastic polymers, ionomer, parylenes, polyamides, polycarbonates, polyesters, polyimides, polyolefins, polyphenylene sulfide, polysulfone, poly(vinyl alcohol) styrenic resin, vinyl resins, plastic alloys, epoxy resins, and polypyrrole.

6. The mixture according to claim 5 herein said polymer is selected from the group consisting of crosslinkable polymers.

7. The mixture according to claim 5 wherein said polymer is water soluble.

8. The mixture according to claim 7 wherein said polymer is selected from the group consisting of poly(vinyl) alcohol (PVOH), a co-polymer comprising PVOH; and a terpolymer comprising PVOH.

9. The mixture according to claim 8 wherein said terpolymer consists of poly(vinylbutyral), poly(vinylacetate) and PVOH.

10. The mixture according to claim 1 wherein said layered filler is a phyllosilicate.

11. The mixture according to claim 10 wherein said phyllosilicate is selected from the group consisting of bentonite, vermiculite, montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, laponite, saucomite, magadiite, kenyomite, ledikite and admixtures thereof.

12. The mixture according to claim 11 wherein said layered filler is vermiculite.

13. The mixture according to claim 9 which comprises in its dried state between about 35% to about 95% by weight PVOH and between 5% to about 55% by weight said layered filler.

14. The mixture according to claim 1 which comprises in its dried state a plasticizer other than water, which is present in a ratio of 1.5 parts by weight polymer to 1 part by weight plasticizer.

15. The mixture according to claim 14 wherein said plasticizer is selected from the group consisting of glucose, polyethylene glycol, ethylene glycol, diethylene glycol, triethylene glycol, glycerine, trimethylol propane, neopentyl glycol, triethanolamine and ethoxylated phosphates.

16. The mixture according to claim 1 comprising a surfactant.

17. An aqueous barrier coating mixture comprising:

- (a) between about 0.25 to 28% by weight of a non-elastomeric polymer, poly(vinyl)alcohol (PVOH);
- (b) between about 0.25 to about 10% by weight of a dispersed exfoliated layered platelet filler, vermiculite, having an aspect ratio greater than 25;
- (c) a plasticizer, glucose; and
- (d) a surfactant,

wherein the solids content of the aqueous mixture is about 6%, and wherein said mixture, when dried, forms a coating comprising about 41% by weight PVOH, about 24% by weight of vermiculite; about 25% by weight of glucose; and about 15% by weight of said surfactant, wherein said coating provides a reduction in gas, vapor or chemical permeability greater than 5-fold that of said dried polymer alone.

18. An aqueous barrier coating mixture comprising:

- (a) between about 0.25 to 28% by weight of a terpolymer consisting of poly(vinylbutyral), poly(vinylacetate) and poly(vinylalcohol);
- (b) between about 0.25 to about 10% by weight of a dispersed exfoliated layered platelet filler, vermiculite, having an aspect ratio greater than 25;

- (c) a plasticizer, glucose; and
- (d) a surfactant,

wherein the solids content of the aqueous mixture is about 6%, and wherein said mixture, when dried, forms a coating comprising about 41% by weight said terpolymer, about 24% by weight of vermiculite; about 25% by weight of glucose; and about 15% by weight of said surfactant, wherein said coating provides a reduction in gas, vapor or chemical permeability greater than 5-fold that of said dried polymer alone.

19. A coated article comprising a substrate having on its surface a dried barrier coating, said coating comprising a polymer and greater than 2% by volume of a layered filler having an effective aspect ratio greater than 25.

20. A coated article comprising a substrate having on its surface a dried coating formed by the coating mixture of any of claims 1-18.

21. The article according to claim 20 wherein said substrate is rigid.

22. The article according to claim 20 wherein said substrate is flexible, highly elastic or elastomeric.

23. A film comprising a dried mixture of a polymer and greater than 2% by volume of a layered filler having an effective aspect ratio greater than 25, wherein said film is characterized by a reduction in gas, vapor or chemical permeability greater than 5-fold the permeability of a film formed of said polymer alone.

24. A film formed by a dried coating mixture of any of claims 1-18.

25. The film according to claim 24 which is in the form of a membrane.

26. A method of reducing the gas, vapor or chemical permeation of a coated substrate, the method comprising:

coating said substrate with an aqueous barrier coating mixture having a solids content of less than about 29% and comprising

(a) between about 0.25 to 28% by weight of a non-elastomeric polymer; and

(b) between about 0.25 to about 10% by weight of a dispersed exfoliated layered platelet filler having an aspect ratio greater than 25; and drying said mixture on said substrate; wherein said mixture, when dried, forms a coating that provides a reduction in gas, vapor or chemical permeability greater than 5-fold that of said dried polymer alone.

27. The method according to claim 26, wherein said solids content is between about 5% and 17%.

28. The method according to claim 26, wherein said mixture, when dried, comprises

(a) said polymer present at a weight percent of at least about 35%; and

(b) said dispersed layered filler present at greater than about 5% by weight, and imparting to said dried mixture an effective aspect ratio greater than 50.

29. The method according to claim 28 wherein said effective aspect ratio is greater than 75.

30. The method according to claim 26 wherein said polymer is selected from the group consisting of acetal, acrylonitrile, acrylic resins, cellulosic plastic, fluoroplastic polymers, ionomer, parylenes, polyamides, polycarbonates, polyesters, polyimides, polyolefins, polyphenylene sulfide, polysulfone, poly(vinyl alcohol) styrenic resin, vinyl resins, plastic alloys, epoxy resins, and polypyrrrole.

31. The method according to claim 30 wherein said polymer is selected from the group consisting of crosslinkable polymers.

32. The method according to claim 30 wherein said polymer is water soluble.

33. The method according to claim 32 wherein said polymer is selected from the group consisting of poly(vinyl) alcohol (PVOH), a co-polymer comprising PVOH; and a terpolymer comprising PVOH.

34. The method according to claim 33 wherein said terpolymer consists of poly(vinylbutyral), poly(vinylacetate) and PVOH.

35. The method according to claim 26 wherein said layered filler is a phyllosilicate.

36. The method according to claim 35 wherein said phyllosilicate is selected from the group consisting of bentonite, vermiculite, montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, laponite, sauconite, magadiite, kenyaite, ledikite and admixtures thereof.

37. The method according to claim 36 wherein said layered filler is vermiculite.

38. The method according to claim 34 wherein said coating mixture comprises in its dried state between about 35% to about 95% by weight PVOH and between 5% to about 55% by weight said layered filler.

39. The method according to claim 26 wherein said coating mixture comprises in its dried state a plasticizer other than water, which is present in a ratio of 1.5 parts by weight polymer to 1 part by weight plasticizer.

40. The method according to claim 14 wherein said plasticizer is selected from the group consisting of glucose, polyethylene glycol, ethylene glycol, diethylene glycol, triethylene glycol, glycerine, trimethylol propane, neopentyl glycol, triethanolamine and ethoxylated phosphates.

41. The method according to claim 26 wherein said mixture comprises a surfactant.

42. A method of reducing the gas, vapor or chemical permeation of a coated substrate, the method comprising:  
coating said substrate with an aqueous barrier coating mixture having a solids content of about 6% and comprising:

- (a) between about 0.25 to 28% by weight of a non-elastomeric polymer, poly(vinyl)alcohol (PVOH);
- (b) between about 0.25 to about 10% by weight of a dispersed exfoliated layered platelet filler, vermiculite, having an aspect ratio greater than 25;
- (c) a plasticizer, glucose; and
- (d) a surfactant; and

drying said mixture on said substrate, wherein said mixture, when dried, forms a coating comprising about 41% by weight PVOH, about 24% by weight of vermiculite; about 25% by weight of glucose; and about 15% by weight of said surfactant, wherein said coating provides a reduction in gas, vapor or chemical permeability greater than 5-fold that of said dried polymer alone.

43. A method of reducing the gas, vapor or chemical permeation of a coated substrate, the method comprising:

coating said substrate with an aqueous barrier coating mixture having a solids content of about 6% and comprising:

(a) between about 0.25 to 28% by weight of a terpolymer consisting of poly(vinylbutyral), poly(vinylacetate) and poly(vinylalcohol);

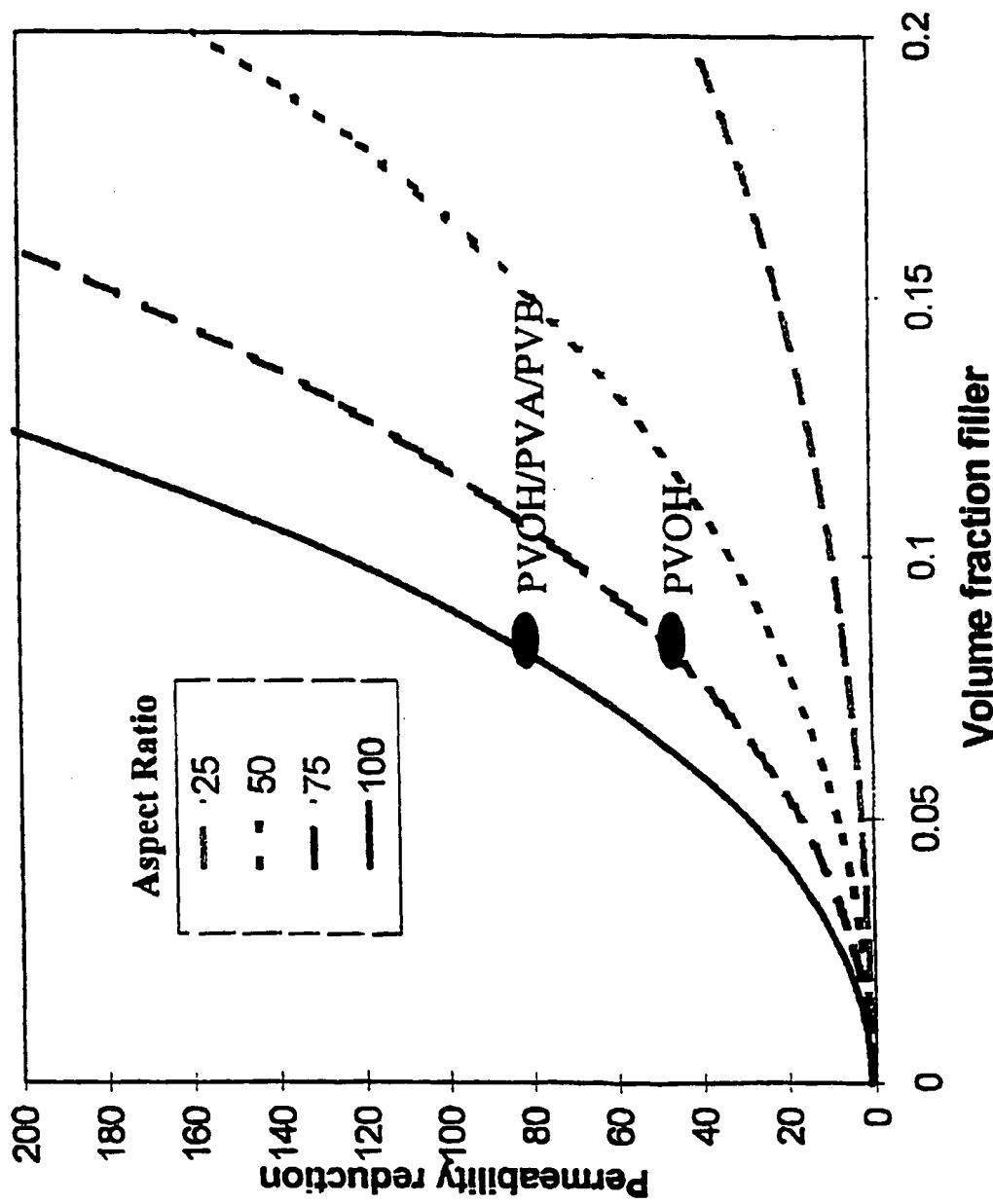
(b) between about 0.25 to about 10% by weight of a dispersed exfoliated layered platelet filler, vermiculite, having an aspect ratio greater than 25;

(c) a plasticizer, glucose; and

(d) a surfactant; and

drying said coating mixture on said substrate, wherein the solids content of the aqueous mixture is about 6%, and wherein said mixture, when dried, forms a coating comprising about 41% by weight said terpolymer, about 24% by weight of vermiculite; about 25% by weight of glucose; and about 15% by weight of said surfactant, wherein said coating provides a reduction in gas, vapor or chemical permeability greater than 5-fold that of said dried polymer alone.

Figure 1



# INTERNATIONAL SEARCH REPORT

Intern  Application No  
PCT/  98/12152

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D1/02 C09D5/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09D C08J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 463 740 A (ICI PLC) 2 January 1992 see claims 1,9,10; tables 3,5 ----	1,19
X	EP 0 518 647 A (ICI PLC) 16 December 1992 see page 4, line 5 - line 21; claim 10; example 4 ----	1-13
X	EP 0 761 739 A (SUMITOMO CHEMICAL CO) 12 March 1997  see claims 1-4; example 10; tables 2-2 ----	1-13,19, 23,24, 26-30, 32-38
X,P	WO 97 47678 A (HOECHST CELANESE CORP) 18 December 1997 see claims 1,17; examples 13-16 ----	1,19  -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 October 1998

Date of mailing of the international search report

12/11/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Schueler, D

## INTERNATIONAL SEARCH REPORT

Intern [REDACTED] Application No  
PCT [REDACTED] 98/12152

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 123 034 A (T & N MATERIALS RES LTD) 25 January 1984 see example 2 ____	1
X	US 4 425 465 A (PADGET JOHN C ET AL) 10 January 1984 see claims 1-11; example 11 ____	1,19
X	US 5 244 729 A (HARRISON ANTHONY G ET AL) 14 September 1993 see example 5 ____	1,19
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 467 (C-550), 7 December 1988 & JP 63 189446 A (SANYO ELECTRIC CO LTD), 5 August 1988 see abstract ____	19
T	"iso2556 plastics-determination of the gas transmission rate of films" 1974, EUROPEAN COMMITTEE FOR STANDARDIZATION, BRUSSELS BE XP002073079 see paragraph TESTREPO - paragraph RT ____	1,19

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

Internal ref. no. Application No.  
PCT/ [REDACTED] 8/12152

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
EP 0463740 A	02-01-1992	CA 2044218 A	DE 69115136 D	DE 69115136 T	21-12-1991 18-01-1996 05-06-1996
		ES 2080250 T	JP 4250035 A	US 5234761 A	01-02-1996 04-09-1992 10-08-1993
EP 0518647 A	16-12-1992	AT 147089 T	AU 648673 B	AU 1821392 A	15-01-1997 28-04-1994 17-12-1992
		CA 2071058 A	CN 1069988 A	CA 2071058 A	15-12-1992 17-03-1993
		DE 69216303 D	DE 69216303 T	DE 69216303 T	13-02-1997 15-05-1997
		DK 518647 T	ES 2096722 T	ES 2096722 T	16-06-1997 16-03-1997
		JP 5177782 A	US 5571614 A	JP 5177782 A	20-07-1993 05-11-1996
EP 0761739 A	12-03-1997	AU 6424296 A	CA 2184308 A	CN 1148062 A	06-03-1997 01-03-1997 23-04-1997
		JP 9124841 A		JP 9124841 A	13-05-1997
WO 9747678 A	18-12-1997	AU 3386397 A			07-01-1998
GB 2123034 A	25-01-1984	DE 3324391 A	FR 2529914 A		12-01-1984 13-01-1984
US 4425465 A	10-01-1984	AT 13686 T	AU 558430 B	AU 8795882 A	15-06-1985 29-01-1987 02-02-1983
		BR 8205347 A	CA 1203333 A	BR 8205347 A	23-08-1983 15-04-1986
		CA 1203333 A	DK 403082 A,B,	CA 1203333 A	15-03-1983
		DK 403082 A,B,	EP 0075396 A	DK 403082 A,B,	30-03-1983
		EP 0075396 A	FI 823141 A,B,	EP 0075396 A	15-03-1983
		FI 823141 A,B,	GR 76283 A	FI 823141 A,B,	04-08-1984
		GR 76283 A	IE 53286 B	GR 76283 A	28-09-1988
		IE 53286 B	JP 1447672 C	IE 53286 B	30-06-1988
		JP 1447672 C		JP 1447672 C	

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

Internal ref.	Application No.
PCT/	8/12152

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 4425465 A		JP 58059267 A		08-04-1983
		JP 62053028 B		09-11-1987
		PT 75552 B		12-12-1984
		ZA 8206444 A		27-04-1983
US 5244729 A	14-09-1993	AT 131088 T		15-12-1995
		AU 645656 B		20-01-1994
		AU 1059492 A		06-08-1992
		CA 2060589 A		05-08-1992
		CN 1065869 A, B		04-11-1992
		DE 69206440 D		18-01-1996
		DE 69206440 T		15-05-1996
		DK 498569 T		22-04-1996
		EP 0498569 A		12-08-1992
		ES 2079791 T		16-01-1996
		JP 5185569 A		27-07-1993